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## Scope of Research

Our research target is to develop high-performance organic electroluminescence devices, organic solar cells, and polymer materials. For the purpose, we have carried out syntheses, device fabrications, precise structure characterizations, and quantum chemical calculations for high functional organic materials. Along with exploring novel synthetic routes and novel devices, detailed analyses of structures and dynamics are performed mainly by sophisticated solid-state NMR spectroscopy in order to obtain structure-dynamics-property relationships.

## KEYWORDS

Solid-State NMR  
Amorphous Materials  
Organic Solar Cells

Organic Light-Emitting Diodes  
Living Radical Polymerization

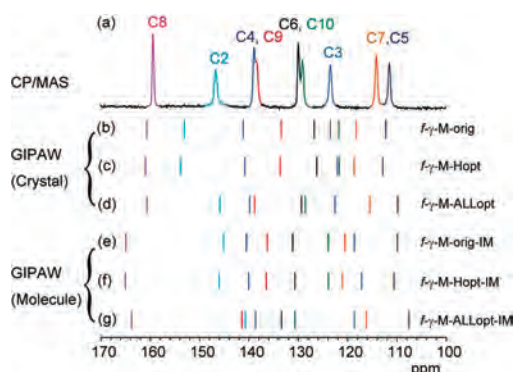
## Selected Publications

- Suzuki, F.; Fukushima, T.; Fukuchi, M.; Kaji, H., Refined Structure Determination of Blue-Emitting Tris(8-hydroxyquinoline) Aluminum(III) (Alq<sub>3</sub>) by the Combined Use of Cross-Polarization/Magic-Angle Spinning <sup>13</sup>C Solid-State NMR and First-Principles Calculation, *Journal of Physical Chemistry C*, **117**, 18809-18817 (2013).
- Hayase, G.; Kanamori, K.; Fukuchi, M.; Kaji, H.; Nakanishi, K., Facile Synthesis of Marshmallow-like Macroporous Gels Usable under Harsh Conditions for the Separation of Oil and Water, *Angewandte Chemie International Edition*, **52**, 1986-1989 (2013).
- Nishiyama, Y.; Fukushima, T.; Fukuchi, M.; Fujimura, S.; Kaji, H., Sensitivity Boosting in Solid-state NMR of Thin Organic Semiconductors by a Paramagnetic Dopant of Copper Phthalocyanine, *Chemical Physics Letters*, **556**, 195-199 (2013).
- Hirata, S.; Totani, K.; Kaji, H.; Vacha, M.; Watanabe, T.; Adachi, C., Reversible Thermal Recording Media Using Time-Dependent Persistent Room Temperature Phosphorescence, *Advanced Optical Materials*, **1**, 438-442 (2013).
- Ohtsuki, A.; Goto, A.; Kaji, H., Visible-Light-Induced Reversible Complexation Mediated Living Radical Polymerization of Methacrylates with Organic Catalysts, *Macromolecules*, **46**, 96-102 (2013).

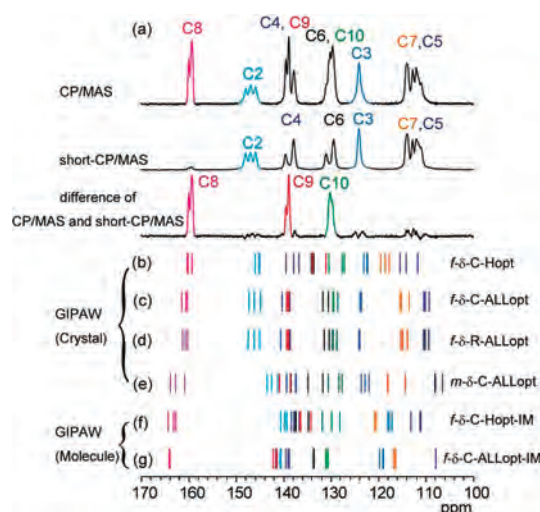


## Refined Structure Determination of Blue-Emitting Tris(8-hydroxyquinoline) Aluminum(III) (Alq<sub>3</sub>) by the Combined Use of Cross-Polarization/Magic-Angle Spinning <sup>13</sup>C Solid-State NMR and First-Principles Calculation

The combined use of cross polarization/magic-angle spinning (CP/MAS) <sup>13</sup>C NMR experiments and gauge-including projector-augmented wave (GIPAW) isotropic chemical shift calculations is an easy and useful method for the structural refinement of organic aggregates. In this study, the method is applied to an important material for organic light-emitting diodes, tris(8-hydroxyquinoline) aluminum(III) (Alq<sub>3</sub>). CP/MAS <sup>13</sup>C NMR spectra include precise structural information of not only the conformation of the molecules, but also the intermolecular packing. First, the structural refinements were performed for the Alq<sub>3</sub> in the  $\gamma$ - and  $\delta$ -crystalline forms employing the combined method. Second, by comparing GIPAW calculations for crystals under periodic boundary conditions and those for isolated molecules extracted from the crystals, information on intramolecular structures and intermolecular structures was distinguished. It was found from the analysis that the  $\gamma$ -Alq<sub>3</sub> and  $\delta$ -Alq<sub>3</sub> crystals have similar intramolecular structures both in the *facial* isomeric state, whereas their intermolecular packing is significantly different. Both the  $\gamma$ -Alq<sub>3</sub> and  $\delta$ -Alq<sub>3</sub> crystals exhibit unusual blue emission, which is different from conventional green emission, and the origin of the difference has been debated. The above investigation shows that the origin of the blue-shifted emission is the isomeric states of Alq<sub>3</sub>, not the intermolecular packing.



**Figure 1.** (a) Experimental CP/MAS <sup>13</sup>C NMR spectrum of  $\gamma$ -Alq<sub>3</sub>. (b)–(g) Isotropic resonance lines of  $\gamma$ -Alq<sub>3</sub> calculated using the GIPAW method. The calculations were carried out for the crystal structures (b) proposed by Muccini et al. without further structural optimization (f- $\gamma$ -M-orig), (c) after the optimization of the atomic coordinates for protons alone (f- $\gamma$ -M-Hopt), and (d) after the optimization of the atomic coordinates for all atoms (f- $\gamma$ -M-ALLopt). Calculations of (e)–(g) were carried out for single molecules extracted from the crystal structures used for the calculations of (b)–(d), respectively.



**Figure 2.** (a) Experimental CP/MAS, short-CP/MAS, and the difference spectra of  $\delta$ -Alq<sub>3</sub>. (b)–(g) Isotropic resonance lines of  $\delta$ -Alq<sub>3</sub> calculated using the GIPAW method. The calculations were carried out for the crystal structures (b) proposed by Cölle et al. after the optimization of the atomic coordinates only for protons (f- $\delta$ -C-Hopt), (c) after the optimization of the atomic coordinates for all atoms (f- $\delta$ -C-ALLopt), (d) proposed by Rajeswaran et al. after the optimization of the atomic coordinates for all atoms (f- $\delta$ -R-ALLopt), and (e) proposed by Cölle et al. after the optimization of the atomic coordinates for all atoms (m- $\delta$ -C-ALLopt). All Alq<sub>3</sub> molecules are in *facial* form in (b)–(d) and in *meridional* form in (e). Calculations of (f) and (g) were carried out for single molecules extracted from the crystal structures used for the calculations of (b) and (c), respectively.

## Visible-Light-Induced Living Radical Polymerization with Organic Catalysts

A photo-induced living radical polymerization (photo-LRP) using organic catalysts was developed. It is among the most simple and robust photo-LRPs, as it uses iodine as a capping agent and the catalysts are such common compounds as tributylamine. Under visible-light-irradiation at 350–600 nm, the polymer molecular weight and its distribution ( $M_w/M_n = 1.1$ – $1.4$ ) were well controlled for methyl methacrylate and some functional methacrylates up to fairly high conversions in many cases. Perfectly no polymerization took place without photo-irradiation, meaning that the system is an ideal polymerization switched “on” and “off” by external photo-stimulus. The polymerization rate was also finely tunable by the external irradiation power. The uses of inexpensive compounds and visible light, good polydispersity control, good tolerance to functional groups, and fine response to external photo-irradiation may be useful features of this system.